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(56) References cited :
DE-A- 2 019 972
DE-A- 2 653 448
GB-A- 1 481 961
JOURNAL OF THE SCIENCE OF FOOD AND AGRICULTURE, vol. 26, no. 2, 1975, pages 219-228, Society of Chemical Industry, Oxford, GB; M.K. WOOLFORD: "Microbiological screening of the straight chain fatty acids (C1-C12) as potential silage additives"
SOVIET INVENTIONS ILLUSTRATED, week C26, 6th August 1980, astract no. 45985C/26, Derwent Publications Ltd, London, GB; & SU-A-697 129 (POLT PIG BREEDING) 28-11-1977

(56) References cited :
JOURNAL OF THE SCIENCE OF FOOD AND AGRICULTURE, vol. 26, no. 7, 1975, pages 941-948, Society of Chemical Industry, Oxford, GB; Y. OHYAMA et al.: "The effect of some additives on aerobic deterioration of silages"

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Description

The present invention relates to a composition for use in silage preparation which enables the enhancement of residual sugars during fermentation of silage.

Formic acid is well known to be an excellent silage additive. The acid, usually at about 80%w/w concentration in aqueous solution, is usually applied on the substrate to be ensiled at the rate of about 2-4 litres per ton. At these levels lactic acid fermentation occurs. In order to restrict the fermentation process and to enhance the residual sugar content of the ensiled substrate e.g. grass, it is necessary to increase the application rate of formic acid (85%w/w) to about 6 litres per ton.

However, increasing formic acid in silage not only makes the silage less palatable to the animals but inevitably increases acidity of the silage thereby causing corrosion problems during storage etc. Moreover, formic acid has relatively low antimicrobial activity and hitherto this has been mitigated by the use of various quantities of sterilants such as e.g. formaldehyde.

In the prior art DE-A-2,653,448 describes as ensiling agent aqueous solutions of complex acid salts of various C_2-C_8 aliphatic carboxylic acids which have from 2 to 4 chemical equivalents of formate ion per cation. Again, the Journal of the Science of Food & Agriculture, vol 26, No. 2, 1975, pp 219-228 discloses inter alia caprylic acid as having potential as a silage additive but suggests that octanoic acid is relatively ineffective on lactic acid bacteria at pH 4 (see Table 3). Neither of these suggest the use of the specific combination of formic acid and octanoic acid as an ensiling composition.

It has now been found unexpectedly that a higher carboxylic acid when used together with formic acid in appropriate proportions can mitigage these effects.

Accordingly, the present invention relates to an aqueous composition suitable for use as an ensiling agent comprising a combination of formic acid and octanoic acid.

The relative proportions of formic acid and octanoic acid in the composition are suitably such that for every 100% w/w of an aqueous solution of formic acid (containing 85% w/w formic acid) there is present suitably from 0.5-10% w/w, preferably from 2-8% w/w of octanoic acid.

The composition is most suitable for ensiling substrates and is preferably applied to the substrate in an amount ranging from 0.35 to 0.9% w/w, most preferably from 0.4-0.7% w/w of the substrate.

The compositions of the present invention may contain in addition other components including propionic acid and ammonia depending upon the activity desired. For instance in a formulation containing both these additional components, formic acid and octanoic acid, the ratio of propionic acid to octanoic acid is suitably at least 2 : 1 w/w, preferably from 3 : 1 to 5 : 1 w/w; and the molar ratio of formic acid to ammonia in said composition suitably is at least 4 : 1, preferably from 4 : 1 to 8 : 1, typically 6 : 1.

Thus a typical composition of this type may contain 75.7% w/w of an aqueous solution of formic acid (corresponding to 64.345%w/w actual formic acid), 10.0% w/w propionic acid, 2.0% w/w octanoic acid and 12.3% w/w aqueous ammonia. (corresponding to 4.06% w/w actual ammonia).

The composition may be applied to the substrate either by direct mixing of the harvested substrate with the ensiling formulation or by impregnating a particulate and porous carrier material such as pumice, vermiculite, perlite dried beet pulp or dried citrus pulp with the formulation and then uniformly distributing the impregnated carrier into the substrate to be ensiled.

Thus, according to a further embodiment the present invention is a process for ensiling substrates as hereinafter defined, said substrate being treated with an aqueous composition by mixing said composition comprising a mixture of formic acid and octanoic acid thoroughly with the substrate to be ensiled.

By the term "substrate" is meant here and throughout the specification grass, agricultrual crops and whole plant materials used in preparing animal feedstuffs such as grass, lucerne, alpha alpha, barley, wheat, oats, rye, maize, rice, hay, silage, tick beans, soya beans, sunflower seed, rape seed, groundnuts.

A feature of the invention is the synergistic effect observed by using a combination of these acids whereby the C_8 acid not only aids inhibition of the rapid fermentation induced by relatively low levels of formic acid so as to reduce levels of lactic acid formed and enhance residual sugars in the ensiled substrate but also confers a preservative antimicrobial effect on the substrate treated.

Moreover, the level of formic acid addition can be reduced in spite of the C_8 acid which, when used alone, has little or no known ensiling or fermentation activity.

The present invention is further illustrated with reference to the following example and accompanying graph.

Example 1

The experiments reported below were designed to compare he effect of (i) formic acid (85%w/w aqueous

solution) applied at 1,3,5 and 7 litres/t, alone and (ii) as a blend thereof with octanoic acid on the biochemicals changes occurring during the ensilage of lucerne

(Medicago sativa).

The residual sugars (water soluble carbohydrates) found in the silage after 100 days peaked at the application rate of 5 litres/t. At these levels fermentation of the silage was clearly restricted and the inclusion of octanoic acid (5%w/w) increased the efficacy of the additive. This is graphically shown in Figure 1.

Examples 3 and 4 (Laboratory Scale):

During the natural fermentation process of ensilage, the desirable sugars found in grass are converted to undesirable lactic acid by the epiphytic microflora. This results in the production of a forage that is deficient in the desirable sugars and therefore the efficiency of utilisation by the animal is reduced. The formulations of the present invention were developed specifically to suppress this natural fermentation process and therefore enable these feedstuffs to retain many of the nutritional advantages of fresh grass feed.

The following Examples 2, 3 and 4 demonstrate this effect. In these Examples the ensiling formulation used contained:

Aqueous formic acid	- 75.7%w/w (64.345%w/w actual formic acid)
Propionic acid	- 10.0%w/w
Octanoic acid	- 2.0%w/w
Aqueous ammonia	- 12.3%w/w (4.06%w/w actual ammonia).

Example 2 (Farm Trial):

The study was carried out on a dairy farm.

A total of 1300 tonnes of grass was ensiled on 3rd July, 1989 with approximately 500 tonnes treated with the formulations specified above at 6 litres/tonne level by thoroughly mixing the formulation with the chopped grass as it was being harvested. The remainder was left untreated. In both cases the grass was stored under substantially anaerobic conditions for 50 days.

Thereafter the ensiled samples were analysed for standard nutritional parameters using the techniques described in "The Analysis of Agricultural Materials", Ministry of Agriculture Food and Fisheries, RB 427, 2nd Edition, published in 1981 by Her Majesty's Stationery Office, London. The appropriate pages relevant for the specific analyses are indicated, where applicable, in the Tables below:

Results

	TREATED*	UNTREATED	PAGE REF
Dry Matter (%)	39.3	35.2	74
pH	4.4	4.1	87
Ammonia N as % Total N	5	5	Steam distillation
Crude Protein	15.5	12.9	130
Mad Fibre	53.6	55.9	82
Ash	7.9	7.6	16
Sugars	20.5	6.3	36
Digestibility (estimate)	58	63	-
Lactic acid	0.96	8.03	204

* According to the invention.

The formulations of the present invention restricted the natural fermentation process producing a forage high in residual sugar and low in fermentation products e.g. lactic acid.

The following Examples 3 and 4 were carried out in a laboratory. Fresh grass was ensiled in mini silos (5kg) by mixing the grass in chopped form with the formulations referred to above using commercial mixing

equipment. The mixture was ensiled in anaerobically sealed containers for 80 days under ambient conditions. The container was then opened and the contents sampled for analysis as previously stated in Example 2 above.

Example 3

Results

	TREATED*	UNTREATED	PAGE REF
Dry Matter (%)	22.4	21.8	74
pH	4.8	4.0	87
Ammonia N as % Total N	10	10	Steam distillation
Crude Protein	14.2	13.6	130
Mad Fibre	58.0	53.1	82
Ash	12.5	13.1	16
Sugars	13.5	1.4	36
Digestibility (estimate)	54	56	-
Lactic acid	0.00	7.56	204

* According to the invention.

The formulations according to the invention restricted the natural fermentation process producing a forage high in residual sugar and no detectable fermentation products (lactic acid).

Example 4

Results

	TREATED*	UNTREATED	PAGE REF
Dry Matter (%)	32.0	32.1	74
pH	4.2	4.1	87
Ammonia N as % Total N	7	7	Steam distillation
Crude Protein	19.9	19.0	130
Mad Fibre	51.3	49.8	82
Ash	18.5	18.0	16
Sugars	6.1	2.0	36
	TREATED*	UNTREATED	PAGE REF
Digestibility (estimate)	52	53	-
Lactic acid	3.55	5.86	204

* According to the invention.

The formulations according to the present invention restricted the natural fermentation process producing a forage high in residual sugar and low in fermentation products e.g. lactic acid.

Claims

1. An aqueous composition suitable for use as an ensiling agent comprising a combination of formic acid and octanoic acid.

2. A composition according to Claim 1 wherein the aqueous solution has from 10 to 50%w/w of water.

3. A composition according to Claim 1 or 2 wherein said composition contains 0.5-10%w/w of octanoic acid per 100%w/w of aqueous formic acid, which contains 85%w/w of formic acid.

4. A composition according to any one of the preceding Claims wherein said composition comprises formic acid, propionic acid, octanoic acid and ammonia.

5. A composition according to Claim 4 wherein the ratio of propionic acid to octanoic acid is at least 2:1 w/w; and the mole ratio of formic acid to ammonia is at least 4:1.

6. A composition according to Claim 4 or 5 wherein the composition comprises:

aqueous formic acid	- 75.7%w/w (64.345%w/w actual formic acid)
propionic acid	- 10.0%w/w
octanoic acid	- 2.0%w/w and
aqueous ammonia	- 12.3%w/w (4.06%w/w actual ammonia).

7. A process for ensiling a substrate with a composition according to any one of the preceding Claims wherein said formulation is applied to the substrate by impregnating a porous particulate carrier material with the composition and uniformly distributing the impregnated carrier in the substrate to be ensiled.

8. A process for ensiling a substrate according to Claim 7 wherein the carrier material is selected from pumice, vermiculite, perlite, dried beet pulp and dried citrus pulp.

9. A process for ensiling a substrate with a composition according to any one of the preceding Claims 1-6 wherein said substrate is treated with the aqueous composition by mixing said composition throughly with the substrate to be ensiled.

10. A process according to Claim 7, 8 or 9 wherein the substrate is a whole plant material selected from one or more of grass, lucerne, alpha alpha, maize, rice, hay, silage, tick beans, soya beans, sunflower seed, rape seed and groundnuts.

Patentansprüche

1. Wäßrige Zusammensetzung mit Eignung zur Verwendung als ein Siliermittel, umfassend eine Kombination aus AMeisensäure und einer Octansäure.

2. Eine Zusammensetzung nach Anspruch 1, wobei die wäßrige Lösung 10 bis 50 % (g/g) Wasser enthält.

3. Zusammensetzung nach Anspruch 1 oder 2, wobei die Zusammensetzung 0,5 bis 10 % (g/g) Octansäure pro 100 % (g/g) der 85 % (g/g) Ameisensäure enthaltenden wäßrigen Ameisensäure enthält.

4. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei die Zusammensetzung Ameisensäure, Propionsäure, Octansäure und Ammoniak umfaßt.

5. Zusammensetzung nach Anspruch 4, wobei das Verhältnis Propionsäure/Octansäure mindestens 2/1 (g/g); und das Molverhältnis Ameisensäure/Ammoniak mindestens 4/1 betragen.

6. Eine Zusammensetzung nach Anspruch 4 oder 5, wobei die Zusammensetzung folgende Stoffe umfaßt:

wäßrige Ameisensäure	75,7 % g/g (64,345 % g/g reine Ameisensäure)
Propionsäure	10,0 % g/g
Octansäure	2,0 % g/g und
wäßrigen Ammoniak	12,3 % g/g (4,06 % g/g reinen Ammoniaks).

7. Ein Verfahren zum Silieren eines Substrats mit Hilfe einer Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei die Rezeptur durch Benetzen eines porösen partikelförmigen Trägermaterials mit der Zusammensetzung und gleichförmiges Verteilen des benetzten Trägers in dem zu silierenden Substrat auf das Substrat angewendet wird.

8. Ein Verfahren zum Silieren eines Substrats nach Anspruch 7, wobei das Trägermaterials aus Binsstein, Vermiculit, Perlit, getrockneten Rübenschnitzeln und getrockneten Zitrusschnitzeln ausgewählt ist.

9. Ein Verfahren zum Silieren eines Substrats mit einer Zusammensetzung nach einem der vorhergehenden Ansprüche 1 bis 6, wobei das Substrat durch gründliches Mischen der Zusammensetzung mit dem zu silierenden Substrat mit der wäßrigen Zusammensetzung behandelt wird.

10. Ein Verfahren nach Anspruch 7, 8 oder 9, wobei es sich bei dem Substrat um ein aus der Gruppe Gras, Luzerne, Alpha, Mais, Reis, Heu, Trockenfutter, Saubohnen, Sojabohnen, Sonnenblumensamen, Rapssamen und Erdnüsse gewähltes Material aus ganzen Pflanzen handelt.

Revendications

1. Composition aqueuse convenant pour emploi comme agent d'ensilage, comportant une combinaison d'acide formique et d'acide octanoïque.

2. Compositiion selon la revendication 1, dans laquelle la solution aqueuse a une proportion d'eau de 10 à 50% en poids.

3. Composition selon la revendication 1 ou 2, dans laquelle ladite composition contient 0,5-10% en poids d'acide octanoïque pour 100% en poids d'acide formique aqueux qui contient 85% en poids d'acide formique.

4. Composition selon l'une quelconque des revendications précédentes dans laquelle ladite composition comporte de l'acide formique, de l'acide propionique, de l'acide octanoïque et de l'ammoniaque.

5. Composition selon la revendication 4, dans laquelle le rapport de l'acide propionique à l'acide octanoïque est d'au moins 2 : 1 en poids et dans laquelle le rapport molaire de l'acide formique à l'ammoniac est d'au moins 4 : 1.

6. Composition selon la revendication 4 ou 5 dans laquelle la composition comporte:

Acide formique aqueux	- 75,7% en poids (64,345% en poids d'acide formique réel)
Acide propionique	- 10,0% en poids
Acide octanoïque	- 2,0% en poids
Ammoniaque	- 12,3% en poids (4,06% en poids d'ammoniac réel).

7. Procédé d'ensilage d'un substrat avec une composition conforme à l'une quelconque des revendications précédentes dans lequel on applique ladite formulation au substrat en imprégnant de la composition un matériau support particulaire poreux et en distribuant uniformément sur le substrat à ensiler le support imprégné.

8. Procédé d'ensilage d'un substrat selon la revendication 7 dans lequel on choisit le matériau support parmi la pierre ponce, la vermiculite, la perlite, la pulpe de betterave sèche, et la pulpe de citron sèche.

9. Procédé d'ensilage d'un substrat avec une composition conforme à l'une quelconque des revendications 1-6 dans lequel on traite ledit substrat avec la composition aqueuse en mélangeant à fond ladite composition avec le substrat à ensiler.

10. Procédé selon la revendication 7, 8 ou 9 dans lequel le substrat est un produit herbacé complet choisi parmi un ou plusieurs des produits suivants, herbe, luzerne, graminées, maïs, riz, foin, fourrage, fèveroles, fèves de soja, graines de tournesol, graines de colza et glands.

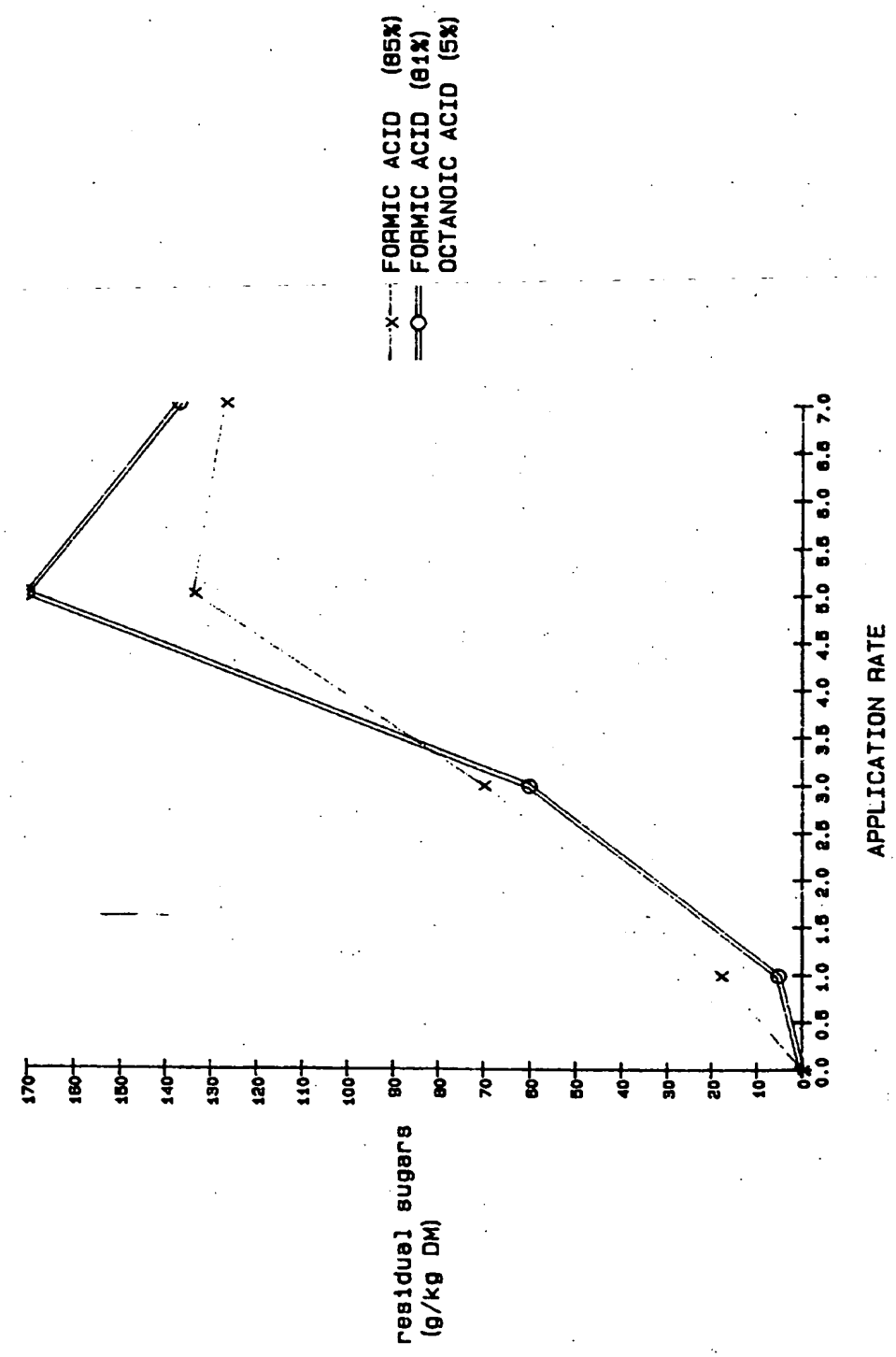

FIGURE 1.
EFFECT OF THE INCLUSION OF OCTANOIC ACID ON THE PERFORMANCE OF FORMIC ACID AS A SILAGE ADDITIVE TO INCREASE RESIDUAL SUGARS